Comments on Fermi Pressure Shift of High-Series Alkali Spectral Lines*

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Abstract

In a recent paper, Choudhury Phys. Rev. $\underline{186}$, 66(1969) obtains an additional term proportional to σ in the Fermi's result for the pressure shift of high-series alkali spectral lines. We show that the term is due to an incomplete understanding of the electron-neutral atom scattering and erroneous approximations in the second order perturbation theory formula employed. A consistent reduction of the Hamiltonian leads to a similar equation considered earlier by Mittleman to investigate the Fermi shift. From the formula derived we present some new estimates on the scattering length, A, for He, Ne and A.

I. Introduction

This paper has arisen out of a critical examination of the present status of Fermi Shift in literature.[1,2,5] The phenomenon of the shift of high members of the principal series of alkali atoms in the presence of foreign gases under pressure has received continued attention since the early nineteen thirties. A part of the shift is attributed to the polarization of the medium (foreign gases) due to the separated valence electron in a high quantum number orbit and the alkali ion and can be understood in a simple fashion. There is another part of the shift which is due to the collision of a very low energy electron with the foreign atoms. This part of the shift turns out to be approximately proportional to the density of the foreign atoms and the scattering length, supporting the experimental observations. Inversally the experimental results can be used to estimate the density of the foreign atoms or alternately the electron scattering cross sections of foreign atoms. Fermi's treatment relates the scattering length and subsequently the scattering cross section at exactly zero energy of the electron. But as n the principal quantum number of the valence electron varies between 20 and 30, the kinetic energy of the hydrogenic electron varies between 0.034 and 0.015 e.volts. Consequently some authors have tried to relate the experimentally observed shifts to the energy dependent cross sections.

Our attention to this problem has been drawn through the work of Choudhury.[1] He defines the problem through a complete Hamiltonian written for one alkali atom and N spherically symmetric foreign atoms, and attempts to treat the various interactions in perturbation theory. Due to a lack of understanding of the electron-neutral atom scattering and some erroneous approximations in the second order perturbation theory formula, he obtains an additional term proportional to the scattering cross section σ in his result. In Sec. II, starting with his Hamiltonian and going through proper approximations we derive the result of Eq. (2.17), which happens to be similar to an equation considered by Mittleman[5] in a reinvestigation of the phenomenon of Fermi shift. Our Eq. (2.17) is superior in its explicit derivation of the valence electron-neutral foreign atom interaction potential. In Sec. III we apply the Fermi's averaging process, as developed by Mittleman,[5] to this equation and derive the formula for the shift. In Sec. IV this formula is used to predict zero energy scattering lengths employing better known values of dipole polarizabilities, but using earlier experimental results on Fermi shift. Our results are similar to O'Malley's[7] calculations, but improved in pertinent ways.

II. Alkali - Foreign Atoms Schrödinger Equation.

Following Choudhury[1] we write the Schrödinger Equation for a system of one alkali atom and N foreign atoms (hence forth called F.A.'s) as

$$\left[H_v + H_c + \sum_{m=1}^{N} \left(H_{Ic}^{(m)} + H_{IV}^{(m)} + H_F^{(m)} + T^{(m)} \right) \right] \Psi = E \Psi , \qquad (2.1)$$

where H_v is the Hamiltonian of the valence electron, H_c that of the alkali core and $H_F^{(m)}$ of the mth F.A. $T^{(m)}$ is the kinetic energy operator of the mth F.A., $H_{IV}^{(m)}$ and $H_{IC}^{(m)}$ represent the interaction energy of the mth F.A. with the valence electron and the alkali core respectively. Except for certain simplifications introduced to ease the algebraic manipulations, we have retained the coordinates and notations defined in I. Taking account of only the Coulomb interaction between the charges, the interaction energy $H_{IC}^{(m)}$ happens to be

$$H_{IC}^{(m)} = \frac{Z Z_f e^2}{R_m} + \sum_{i=1}^{Z-1} \sum_{\ell=1}^{Z_f} \frac{e^2}{\left| \vec{R}_m + \vec{\rho}_\ell^{\,m} - \vec{r}_i \right|}$$

$$- \sum_{\ell=1}^{Z_f} \frac{Z e^2}{\left| \vec{R}_m + \vec{\rho}_\ell^{\,m} \right|} - \sum_{i=1}^{Z-1} \frac{Z_f e^2}{\left| \vec{R}_m - \vec{r}_i \right|} , \qquad (2.2)$$

where $\vec{R}_m$ is the internuclear vector to the mth F.A., $\vec{r}_i$ are the position vectors of the electrons in the Alkali atom and $\vec{\rho}_\ell$ are the position vectors of the electrons in the foreign atom.

In this problem it is assumed that the charge clouds of the Alkali and the F.A. do not overlap and thus a Taylor expansion about R_m can be made. Retaining terms only upto order R^{-3} we get

$$
\begin{aligned}
H_{Ic} = {} & e^2 \sum \frac{\vec{P}_\ell \cdot \vec{R}}{R^3} - e^2 \sum_{i=1}^{Z-1} \sum_{\ell=1}^{Z_f} \sum_{j,k=1}^{3} x_{ij}\, \rho_{\ell k} \Bigg[\\
& - \frac{\delta_{jk}}{R^3} + \frac{3 X_j X_k}{R^5} \Bigg] - \frac{1}{2} e^2 \sum_{\ell=1}^{Z_f-1} \sum_{j,k=1}^{3} \rho_{\ell j}\, \rho_{\ell k} \Bigg[\\
& - \frac{\delta_{jk}}{R^3} + \frac{3 X_j X_k}{R^5} \Bigg] + O(R^{-4}) + \cdots, \quad (2.3)
\end{aligned}
$$

where subscript or superscript m has been dropped and definitions $\vec{r}_i = (x_{i1},\, x_{i2},\, x_{i3})$, $\vec{\rho}_\ell = (\rho_{\ell 1},\, \rho_{\ell 2},\, \rho_{\ell 3})$ and $\vec{R} = (X_1,\, X_2,\, X_3)$ introduced. We have redone this expansion to bring out the third term in Eq.(2.3) for the sake of record as reference I somehow missed it in his Eq. I (2.6). It so happens that only the first term of order R^{-2} gives any significant contribution to the energy shift of the high members of the Alkali spectra in the presence of spherically symmetric F.A.'s. Another reason for correctly writing down the expansion is in the belief that terms of order (R^{-3}) are important in the explanation of red and violet satellite bands observed in the vicinity of low members of the Alkali spectra under similar conditions. We are hoping to elaborate on this point in a subsequent paper.

In Eq. (2.1) it has been possible to divide the interaction of the Alkali atom with the F.A.'s in two parts in treating only the very high quantum number orbits for the electron. Assuming that the charge clouds of the Alkali atom core and the F.A.'s do not overlap, one can use the expansion of Eq. (2.3) and treat the term $\sum_m H_{IC}^{(m)}$ as a perturbation on the zeroth order Hamiltonian

$$H_V + H_c + \sum_{m=1}^{N} \left(H_F^{(m)} + T^{(m)} \right),$$
(2.4)

in Eq. (2.1). For low densities and spherically symmetric F.A.'s, the first term in Eq. (2.3) gives the first non-zero contribution in second order perturbation theory as

$$\Delta E_p(I) = - \frac{2\pi e^2 \alpha_F N}{hc \, r_m},$$
(2.5)

evaluated by Choudhury in Eq. I (4.10). r_m, the impact diameter is a characteristic length dependent upon the impact radius of the Alkali ion and the F.A. and the polarizability α_F. Fermi's method[2] gives this shift by averaging over the polarizable F.A.'s as

$$\Delta E_p(\text{Fermi}) = - \frac{3}{2} \alpha_F \left(\frac{4\pi}{3} \rho_F \right)^{4/3} e^2.$$
(2.6)

In Sec. IV we discuss that adoption of Eq. (2.5) would lead to difficulties in explaining the experimental results.

Replacing the interaction $\sum_m H_{IC}{}^{(m)}$ by ΔE_P in Eq.(2.1) one gets

$$\left[H_V + H_C + \sum_m{}' \left(H_F^{(m)} + T^{(m)} + H_{IV}^{(m)} \right) \right] \Psi = \left(E - \Delta E_P \right) \Psi. \quad (2.7)$$

Now assuming that the Alkali core stays in its ground state defined by

$$H_C \chi_\xi = E_\xi \chi_\xi \quad ,$$

we are able to reduce Eq.(2.1) to

$$\left[H_V + \sum_m{}' \left(H_F^{(m)} + T^{(m)} + H_{IV}^{(m)} \right) \right] \psi = \left(E' - \Delta E_P \right) \psi , \quad (2.8)$$

where

$$E' = E - E_\xi \quad , \quad \text{and} \quad \psi = \left\langle \chi_\xi \mid \Psi \right\rangle.$$

In Eq.(2.8) we have brought in the polarization effect of Fermi due to the ionized Alkali core. There is a similar contribution due to the negative charge of the valence electron and will be brought in at a later stage. In considering the interaction of the valence electron with the F.A.'s it is necessary to consider the possibilities of penetration of F.A.'s charge cloud. H_V is the Hydrogenic Hamiltonian and for orbits of large quantum numbers "n" equal to 20 to 30 the electron kinetic energy varies from 0.034 to 0.015 electron volts. At ordinary temperatures the electron speed is much greater than the speed of the F.A.'s and it is possible to consider the F.A.'s fixed in position. One may then visualize the valence electron of a low kinetic energy scattering from the F.A.'s more or less uniformly distributed in the medium.

Keeping this scattering effect in mind and the fact that the first excited state of F.A.'s is several electron volts above the ground state, we reduce Eq. (2.8) in the following fashion. Define a projection operator P, which projects onto the ground state of all F.A.'s as

$$P = |\vec{r}\,\vec{R}\,\nu_0\rangle\langle\nu_0\,\vec{R}\,\vec{r}| \quad, \tag{2.9}$$

where $\vec{R}$ represents the product $\prod\limits_{m=1}^{N} \vec{R}_m$ and $|\nu_0\rangle = \prod\limits_{m=1}^{N} \phi_{\nu_0}^{(m)}$ with

$$H_F^{(m)} \phi_\nu^{(m)} = E_\nu^{(m)} \phi_\nu^{(m)}.$$

With Q = 1-P, Eq. (2.8) that is, $\mathcal{H}\psi = (E' - \Delta E_P)\psi = \mathcal{E}\psi$ can be written as[3]

$$\left[\mathcal{E} - P\mathcal{H}P - P\mathcal{H}Q \frac{1}{E - Q\mathcal{H}Q} Q\mathcal{H}P \right] P\psi = 0. \tag{2.10}$$

Substituting the explicit form of P and Q Eq. (2.10) appears as

$$\mathcal{E}\langle\nu_0\vec{R}\vec{r}|\psi\rangle - \langle\nu_0\vec{R}\vec{r}|\mathcal{H}|\vec{r}'\vec{R}'\nu_0\rangle\langle\nu_0\vec{R}'\vec{r}'|\psi\rangle$$

$$- \sum_{\nu,\nu'(\neq\nu_0)}' \langle\nu_0\vec{R}\vec{r}|\mathcal{H}|\vec{r}'\vec{R}'\nu\rangle\langle\nu\vec{R}'\vec{r}'|\left[\mathcal{E} - Q\mathcal{H}Q\right]^{-1}|\vec{r}''\vec{R}''\nu'\rangle$$

$$\langle\nu'\vec{R}''\vec{r}''|\psi\rangle = 0 \quad, \tag{2.11}$$

where integrations over repeated variables $\vec{r}'$, $\vec{r}''$, $\vec{R}'$ and $\vec{R}''$ are implied. Using the form of Eq. (2.8) and performing a few integrations over δ- functions one gets

$$\Bigg(\mathcal{E} - \sum_{m=1}^{N} \left(E_{\nu_0}^{(m)} + T^{(m)} \right) - H_V(\mathfrak{x}) - \langle \nu_0 | \sum_{m=1}^{N} H_{IV}^{(m)} | \nu_0 \rangle$$

$$- \sum_{\nu, \nu'(\neq \nu_0)} \langle \nu_0 | \sum_{m'=1}^{N} H_{IV}^{(m')} | \nu \rangle \left[\mathcal{E} - \left\{ H_V + \sum_{m=1}^{N} \left(E_{\nu}^{(m)} + T^{(m)} \right) \right\} \delta_{\nu\nu'} \right.$$

$$\left. - \langle \nu | \sum_{m=1}^{N} H_{IV}^{(m)} | \nu \rangle \right]^{-1} \langle \nu' | \sum_{m''=1}^{N} H_{IV}^{(m'')} | \nu_0 \rangle \Bigg) F_{\nu_0} (\vec{x}, \vec{R}_1, \ldots, \vec{R}_N)$$

$$= 0 \ . \qquad (2.12)$$

Sum over ν, ν' means a sum over complete set of states of the

Hamiltonian $\sum\limits_{m} H_F^{(m)}$. More clearly the matrix element

$$\langle \nu_0 | \sum_{m=1}^{N} H_{IV}^{(m)} | \nu_0 \rangle = \int \prod_{m=1}^{N} \phi_{\nu_0}^{(m)*} (\vec{\rho}_1^{\,m}, \vec{\rho}_2^{\,m}, \ldots, \vec{\rho}_{z_f}^{\,m}) \sum_{m'=1}^{N} \sum_{\ell=1}^{z_f} V_m \left(|\vec{R}_m - \vec{x}|, \vec{\rho}_\ell^{\,m'} \right)$$

$$\prod_{m''=1}^{N} \phi_{\nu_0}^{(m'')} (\vec{\rho}_1^{\,m''}, \vec{\rho}_2^{\,m''}, \ldots, \vec{\rho}_{z_f}^{\,m''}) \prod_{m'''=1}^{N} d\vec{\rho}_1^{\,m'''} \, d\vec{\rho}_2^{\,m'''} \ldots d\vec{\rho}_{z_f}^{\,m'''}$$

$$= \sum_{m'=1}^{N} \int \phi_{\nu_0}^{(m')*} (\vec{\rho}_1^{\,m'}, \vec{\rho}_2^{\,m'}, \ldots, \vec{\rho}_{z_f}^{\,m'}) \sum_{\ell=1}^{z_f} V_m \left(|\vec{R}_m - \vec{x}|, \vec{\rho}_\ell^{\,m'} \right)$$

$$\phi_{\nu_0}^{(m')} (\vec{\rho}_1^{\,m'}, \vec{\rho}_2^{\,m'}, \ldots, \vec{\rho}_{z_f}^{\,m'}) \, d\vec{\rho}_1^{\,m'} \, d\vec{\rho}_2^{\,m'} \ldots d\vec{\rho}_{z_f}^{\,m'}$$

$$= \sum_{m'=1}^{N} \langle \nu_0 (m') | V_m (|\vec{R}_m - \vec{x}|) | \nu_0(m') \rangle \ . \qquad (2.13)$$

In Eq. (2.13) $| \nu_0(m') \rangle$ means the ground state of a single F.A.

By the particular definition of the projection operator P it has been possible to keep H_v and $\sum\limits_{m=1}^{N} T^{(m)}$ in their coordinate space forms. We may now drop the term $\sum\limits_{m} T^{(m)}$ from Eq. (2.12) on the assumption that the F.A.'s are fixed in position. Eq.(2.12) simplifies to

$$
\left[\mathcal{E} - H_v(\vec{x}) - \sum_{m=1}^{N} E_{\nu_o}^{(m)} - \sum_{m=1}^{N} \langle \psi_o(m) | V_m | \psi_o(m) \rangle \right.
$$

$$
- \sum_{\nu,\nu'(\neq\nu_o)} \sum_{m',m''=1}^{N} \langle \psi_o(m') | V_{m'} | \psi(m') \rangle \left\{ \mathcal{E} - \left(H_v(\vec{x}) + \sum_{m=1}^{N} E_{\nu}^{(m)} \right) \delta_{\nu\nu'} \right.
$$

$$
\left. \left. - \sum_{m=1}^{N} \langle \psi(m) | V_m | \psi(m) \rangle \right\}^{-1} \langle \psi'(m'') | V_{m''} | \psi_o(m'') \rangle \right] F_{\nu_o} = 0 . \qquad (2.14)
$$

The matrix element $\langle \psi_o(m) | V_m | \psi_o(m) \rangle$ gives a significant contribution for distances $|\vec{R}_m - \vec{x}| < |\vec{\rho}_\ell^m|$ and a negligible one if $|\vec{R}_m - \vec{x}| > |\vec{\rho}_\ell^m|$ because of the leading term in the expansion of $H_{IV}^{(m)}$ for $|\vec{R}_m - \vec{x}| > |\vec{\rho}_\ell^m|$ as given by I(2.13). The last term in Eq.(2.14) includes the interaction of the ground state of the F.A.'s with excited states and of excited with excited states. The matrix elements of the form $\langle \psi(m) | V_m | \psi'(m) \rangle$ where $\nu, \nu' \neq \nu_o$ will be neglected. This amounts to including effects only upto the second order in perturbation theory.

The inverse matrix in the last term is then diagnal and the
term simplifies to the form

$$- \sum_{\nu \, (\nu \neq \nu_o)} \sum_{m'=1}^{N} \frac{\left| \left\langle \nu_o(m') \left| V_{m'} \right| \nu(m') \right\rangle \right|^2}{\mathcal{E} - H_V(\hbar) - \sum_{m=1}^{N} E_\nu^{(m)}} \, F_{\nu_o} . \qquad (2.15)$$

If in Eq.(2.14) the last two terms were treated as perturbation,
the Hamiltonian H_V quantizes the energy *as*

$$\mathcal{E} - \sum_{m=1}^{N} E_{\nu_o}^{(m)} = E_n .$$

For the electron in a particular quantum state "n" one would re-
place $\mathcal{E} - H_V(r)$ in the denominator by $\sum_{m=1}^{N} E_{\nu_o}^{(m)}$ in Eq.(2.15) to get

the exact form of the second order perturbation formula. This
is essentially the idea of the adiabatic approximation in scatter-
ing[4] Considering the scattering of the valence electron from the
N F.A.'s, the above approximation implies that the electron does
not change its state of energy during the collisions[4] In the
matrix element $\left\langle \nu_o(m') \left| V_{m'} \right| \nu_o(m') \right\rangle$ in Eq.(2.15), ν_o with m'
in parenthesis is our notation for the ground state of m'th F.A.,
while in Eq.(2.12), $\left\langle \nu_o \left| \sum_{m=1}^{N} H_{IV}^{(m)} \right| \nu \right\rangle$ involves the
product states of N F.A.'s. The interaction term $\sum_{m=1}^{N} H_{IV}^{(m)}$ is such
that in the matrix element $\left\langle \nu_o \left| \sum_{m=1}^{N} H_{IV}^{(m)} \right| \nu \right\rangle$
the ground state of N F.A.'s is connected to an excited product
state, when only one of the F.A.'s is excited.

The numerator of Eq.(2.15) clearly reflects this. Therefore in the denominator the sum $\sum_{m=1}^{N} E_\nu^{(m)}$ implies that only one of the terms is not equal to E_{ν_0}. We must write $\sum_{m=1}^{N} E_\nu^{(m)} = \sum_{m \neq s} E_{\nu_0}^{(m)} + E_\nu^{(s)}$, where s can take any value between 1 and N and in particular put s=m' in Eq.(2.15), which becomes

$$-\sum_{\nu (\neq \nu_0)}' \sum_{m'=1}^{N} \frac{|\langle \psi_0(m') | V_{m'} | \nu(m') \rangle|^2}{E_{\nu_0}^{(m')} - E_\nu^{(m')}} F_{\nu_0}$$

$$= \frac{e^2}{2} \sum_{m'=1}^{N} \frac{\alpha_F}{|\vec{R}_{m'} - \vec{x}|^4} F_{\nu_0} , \qquad (2.16)$$

for $|\vec{x} - \vec{R}_{m'}| > |\vec{\rho}_\ell^{m'}|$, $\ell = 1, 2, \ldots , z_f$, and

neglecting terms of order $|\vec{r} - \vec{R}_{m'}|^{-3}$ and higher in the expansion of $V_{m'}$. Eq.(2.14) takes the form

$$\left[\mathcal{E} - \sum_{m=1}^{N} E_{\nu_0}^{(m)} - H_\nu(\vec{x}) - \sum_{m=1}^{N} \left(\langle \psi_0(m) | V_m | \psi_0(m) \rangle \right. \right.$$

$$\left. \left. - \frac{e^2}{2} \alpha_F \frac{1}{|\vec{x} - \vec{R}_m|^4} \right) \right] F_{\nu_0} = 0 \qquad (2.17)$$

The above equation closely resembles the equation considered by Mittleman[5] to derive the Fermi shift. In Eq.(2.17) the short range interaction of the electron with the F.A.'s is explicit, while in Mittleman's work this term is at best implicit through his use of the modified effective-range formula of Spruch, O'Malley and Rosenberg[6].

Spruch and collaborators, in a series of papers,[6,7] have made it transparent that in low energy electron-neutral atom scattering, the short range and the long range polarization potentials are equally important. The polarization potential is responsible for a significant contribution to the scattering while without the effectively repulsive short range potential the scattering length would be negative for all rare gases, including He and Ne, cases where we know it should be positive. Looking at the approach of I, one finds that in I(3.15) the polarization contributions have been ignored in the scattering equation, but reappear in the second order energy shift term in I(4.12), where erroneous approximations have been made. The correct approach is the result in our Eq.(2.16). Ref. I does not seem to realize that the medium excited states with only a single excited F.A. are connected to the medium ground state through the perturbation potential.[8] To evaluate the Fermi shift, Eq.(2.17) has to be averaged over the positions of the F.A.'s and in the following section we follow Fermi's method as developed by Mittleman.[5]

III. Fermi Shift

We begin by writing Eq.(2.17) in the form

$$\left[\mathcal{E}' - \Delta E_p + \frac{\hbar^2}{2\mu} \nabla_r^2 + \frac{e^2}{r} - \sum_{m=1}^{N} \upsilon_m \right] F_{\nu_0} = 0, \qquad (3.1)$$

where $\qquad \mathcal{E}' = E' - \sum_{m=1}^{N} E_{\nu_0}^{(m)} \qquad$ and

$$\upsilon_m = \langle \mathcal{Y}_0(m) | V_m | \mathcal{Y}_0(m) \rangle - \frac{e^2}{2} \alpha_F \frac{1}{|\vec{r} - \vec{R}_m|^4} . \qquad (3.2)$$

Within the sphere of influence of one of the F.A.'s, say the mth one, it is expedient to define a coordinate $\vec{q}_m = \vec{r} - \vec{R}_m \equiv \vec{q}$. Eq.(3.1) for this region appears as

$$\left[\mathcal{E}' - \Delta E_p + \frac{\hbar^2}{2\mu} \nabla_q^2 + \frac{e^2}{|\vec{q} + \vec{R}_m|} - \upsilon_m \right] F_{\nu_0} =$$

$$-\frac{e^2}{2} \alpha_F \sum_{m'(\neq m)}' \frac{1}{q_{m'}^4} F_{\nu_0} \quad \underset{\sim}{\sim} \quad \Delta E_p F_{\nu_0} . \qquad (3.3)$$

In the last step the sum $\qquad \sum_{m'(\neq m)}' \frac{e^2}{2} \frac{\alpha_F}{q_{m'}^4}$

has been replaced by its contribution ΔE_p as calculated in Eq. (2.6) taking $N-1 \sim N$ for large N. Thus for the valence electron within the sphere of influence of the mth F.A. we can write the Eq.(3.3) as

$$\left[p^2(q) + \frac{\hbar^2}{2\mu} \nabla_q^2 - \upsilon_m \right] F_{\nu_0}(\vec{q}) = 0, \qquad (3.4)$$

where for $|\vec{q}| \ll |\vec{R}_m|$, $p^2(q)$ is a slowly varying function of $\vec{q}$ and it is possible to treat Eq.(3.4) as the equation describing the scattering of a particle of energy $p^2(q)$ from a centrally symmetric potential.

The electron in the high quantum number orbits possesses a very low kinetic energy and thus only the s-wave projection of Eq.(3.4) need be considered. Eq.(3.4) is similar to the equation (5) of Mittleman,[5] but with the difference that v_m is more accurately given by our Eq.(3.2), which also happens to be the form employed by O'Malley, Spruch and Rosenberg[6] in a series of papers to expound the effective range formula for electron-neutral atom scattering.

The radial part of the s-wave projected solution of Eq.(3.4) will be written as

$$F(q) = \frac{u(q)}{q} \frac{r_o}{u(r_o)} \langle F \rangle, \qquad (3.6)$$

after Ref. 5. r_o is the limit of influence of a single F.A., while $\langle F \rangle$ is the volume averaged part of the wave function. Using the long range part of Eq.(3.2) a volume average is performed on Eq.(3.1) with the result

$$\left(\mathcal{E}' - \Delta E_p + \frac{2}{r} + \nabla_r^2 \right) \langle F \rangle = \frac{4\pi}{3} r_o^3 \rho_F \left[p^2 \right.$$
$$\left. + \frac{3}{r_o} \frac{\partial}{\partial q} \left(\frac{u(q)}{q} \frac{r_o}{u(r_o)} \right)_{q=r_o} - \frac{3\alpha_F}{r_o^4} \right] \langle F \rangle. \qquad (3.7)$$

Rydberg units have been adopted in the above equation. Further reduction of Eq.(3.7) is achieved by assuming an appropriate form for u(q), which is

$$u(q) = \sin(pq + \delta) - \frac{1}{p} \int_q^\infty dq' \sin p(q-q') \cdot v(q'), \qquad (3.8)$$

and after iterating once, it appears as

$$u(q) \approx \sin(pq + \delta) - \alpha_F \frac{\cos(pq + \delta)}{6pq^3} + \alpha_F (2p)^2 \left[\cos(pq - \delta) \cdot \right.$$
$$\left. C(2pq) + \sin(pq - \delta) \cdot S(2pq) \right], \qquad (3.9)$$

where

$$\begin{pmatrix} C(x) \\ S(x) \end{pmatrix} = \int_x^\infty \frac{dx'}{x'^4} \begin{pmatrix} \cos x' \\ \sin x' \end{pmatrix} .$$

Making expansions appropriate to s-wave scattering that is assuming $\tan\delta < p r_o < 1$ and retaining terms to the lowest order one gets

$$\left(\mathcal{E}' - \Delta E_p + \nabla_\lambda^2 + \frac{2}{\lambda} \right) \langle F \rangle = - 4\pi \rho_F \frac{\tan\delta}{p} \langle F \rangle . \qquad (3.10)$$

If the zero energy limit of the quantity $\frac{\tan\delta}{p}$ ($= -A$, where A is the scattering length) is substituted in Eq. (3.10) one gets the Fermi result, that the shift in the energy level of quantum number "n" is

$$\Delta E_n = \Delta E_p + 4\pi\rho_F A , \qquad (3.11)$$

where ρ_F is the density of F.A.'s. As the objective is to bring in the dependence of the shift on the electron kinetic energy, one may logically introduce an expansion for the quantity $\tan\delta/p$. The choice is the effective range expansion for electron-neutral atom scattering exhaustively discussed by O'Malley, Spruch and Rosenberg,[6]

$$\frac{\tan\delta}{p} = - A - \frac{\pi}{3}\alpha_F p - \frac{4}{3}\alpha_F A p^2 \ln\left(\frac{p\sqrt{\alpha_F}}{4} \right) + D p^2 + \cdots . \qquad (3.12)$$

In the derivation of the formula no specific form of the repulsive short range part of v_m is assumed. The long range part $\left(- \alpha_F/q^4 \right)$ is strictly true for distances greater than the order of the size of the atom, but in the derivation of formula (3.12) the validity

of this potential is extended to the origin in order to evaluate
the value of the Wronskian at origin between the scattering
solution at zero and finite energies. These two intuitively
physical assumptions lead to an acceptable form of expansion
in Eq. (3.12) with A and D as parameters to be determined from
experiments.

Given the expansion (3.12) and assuming p as a constant
function Fermi's result for the energy shift of the nth quantum
level is modified as

$$\Delta E_n = \Delta E_p + 4\pi \rho_F \left[A + \frac{\pi}{3} \alpha_F p + \frac{4}{3} \alpha_F A p^2 \ln\left(\frac{p\sqrt{\alpha_F}}{4}\right) \right].$$

$$(3.13)$$

IV. Results and Discussion

The formula (3.13) is different from Mittleman's result in the sense that we have treated $\tan\delta/p$ as a constant perturbation on the hydrogenic potential of Eq. (3.10) leading to a more convenient form for the analysis of experimental data. In numerical calculations we would identify p^2 as the average kinetic energy of the valence electron in the nth quantum orbit of the hydrogen atom. This identification is strictly justifiable for relative distances "q" beyond the range of the potential $\mathcal{V}_m$ of any one F.A.

If one studies the experimental curves[9] of ΔE_n vs: n for a particular temperature and pressure (fixed density of the foreign gas) one notices that ΔE_n becomes practically constant for n beyond about 20. Experimental points are given for n upto 30. Ch'en and Takeo have plotted the experimentally constant shift ΔE (for n ≈ 30. as the limit of the series) against relative density[11] for He, Ne and A among others in Fig. 8 of Ref. 10 and the value of the energy shift (in $cm^{-1}/r.d.$) for He, Ne and A is given by +5.9, +0.2 and -9.7, respectively. It is important to note that these shifts are independent of the absorbing alkali metal employed. To make meaningful comparisons with other theories we would evaluate A, the scattering length, using the formula (3.13) with ΔE_p given by Eq. (2.6) and more recent values of dipole polarizability[12] α_F.

The result of Eq.(2.5) derived by Choudhury makes ΔE_p depend upon the type of alkali metal employed through r_m, the impact diameter. This would in turn make A, the electron-F.A. scattering length vary with various alkali metals contradicting the theoretical assumptions. The results of our calculations are summarized in Table I. In the fourth column we have tabulated the values of A by ignoring the log term in the formula of Eq.(3.13). This is similar to the calculational approach of Ref. 7. For Krypton and Xenon we have used $\Delta E - \Delta E_p$ $(=\Delta_{v\sigma})$ values cited in Ref. 10. To see the effect of the log term on A we have given the factor needed as a divisor in the last column of Table I. The effect is to increase the magnitude of A in all cases increasing the difference between scattering lengths predicted by the pressure shift method and by all other experimental and theoretical approaches listed in Tables 8.8 and 8.9 of Ref. 13.

In conclusion we would like to remark that it appears difficult to predict the low energy structure of scattering cross sections in detail from pressure shift experiments. For high quantum numbers n between 20 and 30, where Fermi theory is valid, the valence electron energy varies between 0.034 and 0.015 e. volts and cross sections can be obtained over this range, but it does not seem possible to observe the Ramsauer effect, which takes place for electron energies between 0.5 and 1 e. volts. The conclusions reached by I are entirely due to erroneous theoretical approximations and a lack of understanding of low energy electron-neutral atom scattering.

Foreign Gas	Dipole Polarizability α_F $\times 10^{-24}$ cm^3	$\Delta E - \Delta E_p$ (cm^{-1}/r.d.)	A (units of a_O)	$1 + \frac{4}{3} \alpha_F p^2 \ln\left(\frac{p\sqrt{\alpha_F}}{4}\right)$
He	0.2051	6.1	1.05	0.9875
Ne	0.367	0.55	0.0024	0.9786
A	1.64	-8.15	-1.913	0.9212
Kr	2.48	-17.2	-3.773	0.9126
Xe	4.04	-31.6	-6.799	0.8325

Table I: Calculations of zero energy scattering length in units of Bohr radii (a_O). The value of $p = 0.04$ corresponding to $n = 25$ has been uniformly employed.

Acknowledgements

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